Theory of Isoperibol Calorimetry for Laser Power and Energy Measurements

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Laser power and energy measurements are commonly made in calorimeters operating in a constant temperature environment. Calorimeters of this type are analyzed in terms of the first law of thermodynamics and the boundary value problem describing heat flow in the calorimeter. This theory of the measurement suggests design features of the calorimeter, sources of error to be avoided in design and operation, and tests to demonstrate experimentally the adequacy of the design. The analysis shows how time–temperature data can be used to allow for the temperature gradient on the calorimeter and the heat exchange due to transients in the temperature.

INTRODUCTION

Laser power and energy measurements are commonly made in calorimeters operating in a constant-temperature environment.[1] Calorimeters of this type subsequently called isoperibol calorimeters,[2] can be studied in terms of the first law of thermodynamics and the boundary value problem which describes heat flow in the calorimeter. The resulting measurement theory suggests possible sources of calorimetric errors, some experimental tests for these errors, and design features which reduce or eliminate these errors.

The usual theory of isoperibol calorimetry[3,4] is derived using the simplifying assumption that the temperature of the calorimeter is uniform, which goes contrary to the practice of waiting to make the final temperature measurement until the observed temperature is a single exponential function of time, that is, until the higher order exponentials are negligible [see Eq. (14) below]. White[3] considers "lags" in the calorimeter in an intuitive way and states that lag effects are accounted for when the calorimeter is calibrated. Our development shows that White's statement must be qualified in important respects.

The heat flow problem leads to an expression for the temperature which involves a series of exponential functions of time. When only one of these exponentials is significant, the observed temperature is a state variable which is a measure of the internal energy of the calorimeter. The heat exchange due to the other exponentials can then be determined if the calorimeter is properly calibrated. When the internal energy of the calorimeter and the heat exchange are known, the electromagnetic work done on the calorimeter by the laser beam can be calculated by the first law. The calculation, summarized in Eq. (20), is made in the same manner prescribed by the usual simplified theory;

an energy equivalent determined in a calibration experiment is multiplied by a "corrected temperature rise." This temperature rise consists of the difference between the final and initial temperatures, which must be observed when the temperature is a single exponential function of time, plus the product of the "cooling constant" and the integral of the temperature-time curve.

Equation (20) and the assumptions made in deriving it form the basis for designing and testing isoperibol calorimeters and for analyzing the data. The resemblance of Eq. (20) to the results of the simple theory conceals an important difference. The simple theory treats heat flow as proportional to a measured temperature difference. If the region connecting the two temperatures measured contains matter, such as a gas, solid supports or electrical leads, then heat flow is proportional to temperature difference only for a steady state temperature distribution. By contrast, Eq. (20) holds for the time-varying temperature distributions actually encountered.

In this analysis, it is shown that the energy equivalent is dependent on the geometrical distribution of the power from the various sources. No systematic error results if the heat generated anywhere inside the calorimeter flows to the surface of the calorimeter by a well-defined path so that the temperature measurement properly accounts for the heat exchange. This "equivalence of sources" should be designed into the calorimeter and checked experimentally to demonstrate that this systematic error is negligible. The experimental check requires calibration with several known sources which generate heat in very different parts of the calorimeter—two electrical heaters in different locations, for example. A calibrating heater presents a special problem because heat is generated in the current leads. For most laser calorimeters it is probably adequate to make the

electrical heater resistance large compared to the resistance of the leads. If necessary, more rigorous tests and mathematical analyses can be used.[5,6]

An assumption in the analysis is that the temperature of the surroundings is constant. Experimentally, the question is what deviations from constancy can be tolerated for the accuracy required. The constant-temperature enclosure for a laser calorimeter must have an opening for the beam to enter, so that there is heat exchange by radiation between the calorimeter and the room. The room thus becomes part of the surroundings where the temperature must be constant and tests are required to show that it is sufficiently constant. Calorimeter design can reduce the effect of the room by placing the calorimeter well away from the opening in the enclosure to minimize the radiant heat exchange with the room. A shutter which closes the opening in the surroundings may have some application.

The effect of changes in the temperature of the surroundings can be checked experimentally by deliberately changing it during a calibration experiment. Its constancy is checked in the analysis of the data [Eq. (14)].

Further checks on the operation of the calorimeter are obtained from the data analysis. The corrected temperature rise, Eq. (20), must be constant for all times after the temperature becomes a single exponential function of time. Constancy of this quantity is a good criterion for the single exponential condition. The cooling constant obtained from Eq. (14) should occasionally be checked for constancy for long times following an energy input. Changes in this quantity over an appreciable time imply deviations from the assumed experimental conditions and possible systematic errors.

Extrapolation techniques for data analysis are attractive because they simplify the analysis and because, for some calorimeters, they may reduce errors due to changes in the temperature of the environment. Extrapolation results in systematic errors when the sources compared generate heat in different parts of the calorimeter or as different functions of time. Both of these effects can be checked experimentally with known sources. If the geometric effect can be neglected, the theory provides a basis for comparison of pulse and cw energy inputs by extrapolation to the time of the pulse and to the midpoint of the cw input.

There are some problems which are common to all measurements of laser energy and power. They deserve mention here to emphasize that there is more to the measurement than proper operation of the measuring device.

Our analysis requires that the composition of the calorimeter remain unchanged. A change in composition is an important consideration for high-power lasers, which may melt or vaporize a surface, cause a surface to oxidize, or excite an absorbing medium which decays slowly to the initial state. All of these changes in composition have appreciable heat effects associated with them. These effects are very hard to find from analysis of the calorimetric data and are preferably eliminated by separate experiments.

There may be errors in collecting the desired radiation and converting it to heat. Some of the energy may be reflected from the calorimeter without absorption, and, in some calorimeters, loss by fluorescence might be appreciable. Because of uncertainties in determining the fraction lost, it seems prudent to design calorimeters for absolute measurements to absorb nearly all the incident radiation. An error of opposite sign is caused by radiation received from extraneous sources, such as a flash lamp for a ruby rod.

Thermal re-radiation from the calorimeter may be a problem if the laser heats the surface of the calorimeter appreciably. A partial solution is to disperse the beam before absorption. In addition, the calorimeter can be designed to absorb most of this thermal re-radiation.

TABLE OF SYMBOLS

a_i	constants which fit the eigenfunctions of the boundary value problem Eq. (5) to the initial condition
B	a closed boundary surrounding the calorimeter where the temperature is unchanged during the experiment
b_i	eigenvalues of the boundary value problem Eqs. (5)
c	heat capacity per unit *volume*
C_1	$= \int c\phi_1 dV$
f	power generated in the calorimeter
g	geometric distribution of a laser or electrical source
g	subscript refers to properties of the gas in the calorimeter
h	coefficient for heat transfer by radiation
k	defined by Eq. (17)
n	unit vector drawn perpendicularly outward from a surface: $\partial T/\partial n = \nabla T \cdot \mathbf{n}$
P	position in an arbitrary coordinate system
p_∞	power constant throughout the experiment
Q	quantity of heat transferred to a thermodynamic system
Q_∞	heat exchange equal to $-W_\infty$
Q'	heat exchange in the transient problem. $Q' = Q - Q_\infty$
S, S'	surfaces which exchange heat by radiation. See Fig. 1
T	temperature—may be thought of as the absolute temperature
T_∞	temperature distribution in the steady-state due to p_∞
T'	$= T - T_\infty$
T^*	the observed temperature

t	time
U	internal energy of a system
V	volume
W	work done on a thermodynamic system
W_∞	work done by constant power sources
W'	work in the transient problem: $W' = W - W_\infty$
α_i	constants which fit the eigenfunctions to an initial condition caused by unit work input with the distribution $g(P)$
β	constant power input for a definite interval
∇	vector differential operator
λ	thermal conductivity
Λ_i	$= \int \lambda(\partial\phi_i/\partial n) dB - \int\int h\phi_i(S') dS dS'$
τ	past time $\tau \leq t$
Φ_i	eigenfunctions of the boundary volume problem Eq. (5)
Φ_i^*	value of the eigenfunction at the position of the thermometer

APPLICATION OF THE FIRST LAW TO CALORIMETRY

In general, a calorimetric measurement is a comparison of a known to an unknown energy, according to the first law of thermodynamics. Application of the first law requires consideration of a boundary of the system, the variables which specify the state of the system, and evaluation of the heat and work quantities.

The boundary required by the first law is restricted only in that it must enclose the two regions where the energies to be compared are converted to heat. However, the subsequent analysis in terms of experimental quantities requires consideration of a boundary value heat flow problem for which we take the boundary to be the constant temperature surface which surrounds an isoperibol calorimeter. The analysis is based on the assumption that the temperature of this surface need only be constant, but not necessarily uniform.

The first law equates the change in the internal energy ΔU of the system to the sum of the heat Q transferred to the system and the work W done on the system

$$\Delta U = Q + W. \tag{1}$$

The important work terms are the electrical work done in a calibration and the electromagnetic work done by the laser beam.

There is some difficulty in distinguishing work quantities from heat quantities. In papers on calorimetry, it is common to speak of the heat of stirring and electrical heat, but, if the calorimeter is treated as a thermodynamic system, it seems clear that both of these are work quantities converted to heat inside the system boundary. With Bridgman,[7] we have used the term work for the radiation in the laser beam. This distinction from heat transfer by radiation is made on the basis that there is no temperature difference associated with the laser radiation.

Equation (1) is the basic means of directly relating the energy in a laser beam to known electrical quantities, which can be accurately expressed in joules, the basic energy unit. To use Eq. (1) for calorimetry, one must provide the experimental methods necessary to specify the state of the system and to evaluate the heat and work terms.

In the simple theory, which treats the calorimeter as uniform in temperature, the specification of the state variables is straightforward. The temperature of a thermometer located anywhere in the calorimeter gives the temperature of the system. The calorimeter is usually operated at atmospheric pressure, and the composition (or physical state) is either constant, as in an electrical calibration, or the change in composition, as in a chemical reaction, for example, is determined in auxiliary experiments. The question of composition in laser calorimeters is not a trivial one; the high power densities available can produce some rather spectacular changes in composition or physical state.

The temperature in real isoperibol calorimeters is not uniform, but the change in the internal energy of the calorimeter may be expressed as the sum of the changes in subsystems so small that their temperatures are uniform to any desired tolerance. The internal energy of these subsystems also depends on their pressures due to thermal stresses. The direct measurement of these temperatures and pressures is manifestly impracticable. What we seek is a relationship between the temperature of each subsystem and the observed temperature. Such a relationship will also specify a unique set of thermal stresses, providing the temperature gradient is too small to cause permanent deformations.

To develop the required temperature relationships, which are also necessary to evaluate the heat exchange, we proceed to a detailed consideration of the heat flow problem.

THE HEAT FLOW PROBLEM

The essential parts of the measurement theory can be deduced from a general heat flow problem which considers both conduction and radiation in a region bounded by a surface at constant, but not uniform, temperature. Heat transfer by convection is excluded because it is nonlinear in the temperature. From the design standpoint, convection is not a problem if spaces and temperature differences are kept small. We proceed to formulate a heat flow problem describing a calorimeter of an arbitrary shape consisting of various solids and gaseous (or evacuated) regions.

The equation for the conduction of heat in the calorimeter can be written in the following quite general form[8,9]:

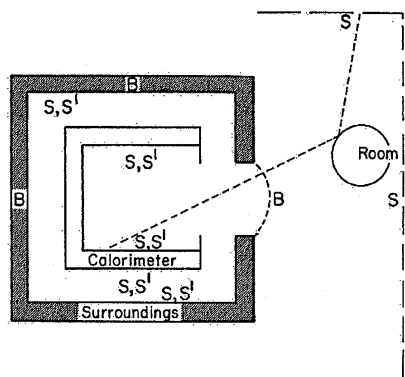$$\nabla \cdot \lambda(P)\nabla T(P,t) = c(P)\partial T/\partial t - p_\infty - g(P)f(t), \tag{2}$$

FIG. 1. Sketch to illustrate bounding and radiating surfaces. The calorimeter is completely enclosed by a boundary B which is at a constant temperature throughout the experiment. Part of B (dotted line) is located somewhere in the air near the opening for the laser beam. The surfaces S and S' are solid-gas interfaces which exchange heat by radiation. They may coincide with B in some areas. S' is located inside the boundary B; S includes surfaces in the room.

where T is the temperature, a function of position, P, and time, t; λ is the thermal conductivity, c is the heat capacity per unit volume, and p_∞ is the constant power developed per unit volume, all functions of position only. The constant power p_∞ includes any nonthermal background radiation through the opening for the laser beam. In the last term $f(t)$ represents the total power generated in the calorimeter and $g(P)$ represents the fraction generated at the position P.

The assumption that both λ and c are independent of temperature requires that operation of the calorimeter be restricted to temperature ranges so small that the variations of λ and c with temperature can be neglected.

Heat is transferred simultaneously by radiation and conduction across gas spaces. Radiation from a given point in an enclosed region can reach any other point in the region by multiple reflections. If absorption of radiant energy by gas is negligible, it can be shown that the radiant heat transfer between any pair of points is fixed by the geometrical arrangement of the space, the optical properties of the surfaces, and the temperatures at the points.[10a] Figure 1 is a sketch to illustrate the various surfaces which exchange heat by radiation. For small temperature differences we can express the rate at which heat is radiated from an infinitesimal area dS' on surface S' to an area dS on surface S by the expression $h(S, S')[T(S') - T(S)]dS'dS$, where $T(S')$ and $T(S)$ denote temperatures on surfaces S' and S respectively. The surface S' includes all solid-gas interfaces inside the boundary B of the calorimeter system. The surface S consists of S' and those surfaces outside B which exchange heat by radiation through the opening for the laser beam. If part of the boundary B is a gas-solid interface, then that part of B is included

in both S and S'. In that case, the temperature $T(B)$ on the boundary will appear in Eq. (3a). In any case, Eq. (3a) will be made homogeneous when the steady-state solution is subtracted (see below). The total rate at which heat is radiated from dS' is obtained by integrating over surface S. The resulting equation for heat flux at a point on the surface S' is

$$-\lambda(\partial T/\partial n) = -\lambda_g(\partial T_g/\partial n)$$
$$+ \int h(S, S')[T(S') - T(S)]dS, \quad \text{(3a)}$$

where the temperature and thermal conductivity of the gas is indicated by subscript g, and $\partial T/\partial n$ is the temperature gradient in the direction of the outward drawn normal to the surface. Physically, Eq. (3a) states that the heat flux at a point on the solid surface is equal to the heat flux into the gas plus the net heat radiated from that point to all points on the surface S. The equation governs heat exchange by radiation through the opening for the laser beam from that part of the surface S outside the calorimeter boundary. In addition to (3a) we require that the temperature be continuous at the solid-gas interface

$$T = T_g. \quad \text{(3b)}$$

On the system boundary, B, the temperature takes on the constant but nonuniform temperature of the surroundings

$$T = T(B) \text{ on } B. \quad \text{(3c)}$$

The laser calorimeter is not completely bounded by a solid surface, because the surroundings must have an opening for the laser beam. For this part of the boundary we take a surface in the gas, which, together with the solid surface, gives a closed boundary for the calorimeter system. We specify that the temperature of the gas is constant on this surface as in (3c). Since there is radiant heat transfer across this surface we require that all temperatures $T(S)$ outside this boundary be constant.

The heat flow problem assumes the temperature of this boundary is constant and the practical problem of whether it is constant enough must be answered by experiment. The obvious way to minimize the problem of the opening is to put the calorimeter well inside the constant temperature enclosure and to make the opening as small as possible. This procedure is desirable in any case to minimize gas conduction from the calorimeter through the opening.

Note that a constant level of light reflected into the calorimeter is included as part of the steady-state power. Light associated with the operation of the laser obviously must be excluded from the calorimeter, either by suitable apertures or by locating the calorimeter a good distance away. The light entering the calorimeter from this source will decrease with distance.

In the absence of a calibrating or a laser input, the temperature in the region bounded by B will eventually

reach a steady-state determined by the temperature distribution on B and any constant power sources, such as light from the room or resistance thermometers. The subscript ∞ will be used to refer to the quantities characteristic of this steady state; the temperature is $T_\infty(P)$, the total heat exchange is Q_∞, and the total work is W_∞. In the steady state, the internal energy is constant so from (1)

$$Q_\infty = -W_\infty = -\int \dot{p}_\infty dt. \qquad (4a)$$

The rate at which heat flows into the calorimeter is the sum of conduction across the boundary of the system and radiation through the opening for the laser beam. The conduction term is just the integral of the heat flux over the entire boundary B; the radiation term is the double integral over the surface S' inside the calorimeter and the surface S, which is S' plus the surfaces which radiate into the calorimeter through the opening. This rate of heat exchange is given by the equation

$$dQ_\infty/dt = \int \lambda (\partial T_\infty / \partial n) dB$$
$$- \int\int h(S, S')[T_\infty(S') - T_\infty(S)] dS'dS. \qquad (4b)$$

Note that the radiation term has no net contribution for the part of S which coincides with S'. To account for an initial temperature distribution, the solution of Eqs. (2) and (3) is given by the superposition of T_∞ and a solution T' of the following boundary value problem

$$\nabla \lambda \nabla T' = c \partial T'/\partial t \qquad (5a)$$
$$-\lambda(\partial T'/\partial n) = -\lambda_g(\partial T_g'/\partial n)$$
$$+ \int h(S, S')[T'(S') - T'(S)] dS, \text{ on } S. \qquad (5b)$$

In (5b), $T'(S) = 0$ when S coincides with B or when S is a surface exchanging heat by radiation through the opening for the laser beam

$$T' = T_g'; \qquad (5c)$$
$$T' = 0 \text{ on } B. \qquad (5d)$$

The initial condition is

$$T' = T(P, 0) - T_\infty. \qquad (5e)$$

The problem is homogeneous and can be solved by separation of variables to give a solution of the form $\Phi(P)e^{-bt}$. A constant a times the product is also a solution. The separation constant b can have different values so that a general solution to the homogeneous problem has the form

$$T' = \sum a_i \Phi_i(P) \exp(-b_i t), \qquad (6)$$

where the a_i are chosen to represent the temperature distribution T' at $t = 0$.

By a procedure analogous to that used by Boley and Weiner,[9] it can be shown from Eqs. (5) that the b_i are real and greater than zero, and that the Φ_i corresponding to different b_i are orthogonal or, in case of degeneracy, have been orthogonalized. We assume that they constitute a complete set and that there is only one Φ corresponding to b_1.[11]

RATING PERIOD AND INTERNAL ENERGY

In time, it is observed, that the temperature is a single exponential function of time; i.e., only one exponential in Eq. (6) is significant

$$T - T_\infty = a_1 \Phi_1 \exp(-b_1 t). \qquad (7a)$$

When this equation holds, we will say that the calorimeter is in a rating period. The same equation applies to the observed temperature T^* which is just the value of the temperature at the point where the measurement is made. If the thermometer occupies an appreciable volume, then T^* is the average over the volume of the sensitive part of the thermometer. For small temperature differences, the response of the thermometer is probably sufficiently linear that the observed temperature is also the average temperature of the sensing element. For the observed temperature, (7a) is written

$$T^* - T_\infty^* = a_1 \Phi_1^* \exp(-b_1 t), \qquad (7b)$$

where ϕ_1^* may represent an average value for the thermometer.

When the temperature as a function of position obeys (7a), it can be written in terms of the observed temperature. Division by (7b) gives the time-independent relationship

$$T - T_\infty = (T^* - T_\infty^*)\Phi_1/\Phi_1^*. \qquad (8)$$

This equation relates the temperature anywhere in the calorimetric system to the observed temperature. The observed temperature is therefore a state variable when it is a single exponential function of time; that is, when the calorimeter is in a rating period.

Using the approximation made in Eq. (2) that the heat capacity is a function of position only, the change in the internal energy of the calorimeter can be written for two temperature distributions T_1 and T_2 at the time t_1 and t_2 respectively

$$\Delta U = \int c[T_2(P, t_2) - T_1(P, t_1)] dV. \qquad (9)$$

If we define a weighted heat capacity $C_1 = \int c\Phi_1 dV$, then, during rating periods, (8) applies and (9) can be written

$$\Delta U = C_1(T_2^* - T_1^*)/\Phi_1^*. \qquad (10)$$

Heat enters the calorimeter by conduction at the boundary and by radiation through the opening for the laser beam. The conduction is the product of the thermal conductivity and the temperature gradient normal to the surface integrated over the conducting part of the surface B, and the radiation is proportional to the

temperature difference, analogous to the integral in (3a), integrated over the radiating surfaces S and S'. The heat entering the calorimeter due to T' is

$$dQ'/dt = (dQ/dt) - (dQ_\infty/dt)$$

$$= \int(\lambda \partial T'/\partial n)dB - \iint hT'(S')dSdS', \quad (11)$$

where dQ_∞/dt is taken from Eq. (4b). Defining the quantities

$$\Lambda_i = \int\lambda(\partial\Phi_i/\partial n)dB - \iint h\Phi_i(S')dSdS', \quad (12)$$

and substituting from (6), Eq. (11) can be written

$$dQ'/dt = \sum a_i\Lambda_i \exp(-b_i t).$$

For a rating period only the first term is significant. By using (7b) this term can be written in terms of the observed temperature

$$dQ'/dt = \Lambda_1(T^* - T_\infty^*)/\Phi_1^*.$$

Differentiating (10) and using (7b) we obtain

$$d\Delta U/dt = C_1(dT^*/dt)/\Phi_1^* = -C_1 b_1(T^* - T_\infty^*)/\Phi_1^*.$$

During rating periods there are no active sources, so from Eq. (1) $d\Delta U/dt = dQ'/dt$. These three relationships give

$$-b_1 C_1 = \Lambda_1, \quad (13)$$

which defines the constant b_1—traditionally called the cooling constant—as the ratio of a heat transfer coefficient to the weighted heat capacity. The constant, b_1, is determined experimentally using the following relationship derived from (7a):

$$\partial T/\partial t = -b_1(T - T_\infty). \quad (14)$$

This relation holds throughout the calorimeter, so that the cooling constant is independent of the location of the thermometer.

THE HEAT EXCHANGE

Equation (1) requires that the heat exchange be evaluated for the entire length of the experiment, which extends through the main part of the experiment when the observed temperature is *not* a measure of the internal energy of the system. Since the heat exchange depends on the temperature gradient throughout the experiment, the expression for the temperature must be developed before the heat exchange can be considered. The temperature will be expressed as the superposition (sum) of the temperature due to the initial condition and the temperature due to a heat source in the calorimeter. The experiment begins with the calorimeter in a rating period, so that the initial temperature distribution is described by the first term in the series (6). The temperature due to a heat source can also be stated in terms of an initial value problem. For concreteness, suppose that, at a time τ, one joule of electric energy is converted to heat in the heater wire in a negligible length of time. The temperature of the heater wire will be raised and the initial value for the temperature for this problem will depend on the location $g(P)$ of the wire and its heat capacity $c(P)$. This problem is the same as the initial value problem (5) but with a time scale beginning at time τ and the initial temperature distribution $g(P)/c(P)$. The constants α_i are chosen to represent this initial temperature distribution at time $t = \tau$. An input $f(\tau)d\tau$ J at time τ will produce a proportionate temperature rise and the total effect of all inputs $f(\tau)$ can be obtained by integration over the past time τ to give the following equation:

$$T - T_\infty = a_1\Phi_1 \exp(-b_1 t)$$

$$+ \int_0^t f(\tau)\sum\alpha_i\Phi_i \exp[-b_i(t-\tau)]d\tau. \quad (15)$$

In (15) $f(t)$ is the time dependence of the source; the geometric dependence $g(P)$ is represented by the products $\alpha_i\Phi_i$. The heat exchange is given by integrating (11) substituting $T' = T - T_\infty$ from (15) using the definitions (12); for a time t in the final rating period when only the first exponential is significant

$$Q' = a_1\Lambda_1 b_1^{-1}[1 - \exp(-b_1 t)]$$

$$+ \alpha_1\Lambda_1 b_1^{-1}\int_0^t f(\tau)\{1 - \exp[-b_1(t-\tau)]\}d\tau$$

$$+ \sum_{i=2}\alpha_i\Lambda_i b_i^{-1}\int_0^t f(\tau)d\tau. \quad (16)$$

The integral of $f(\tau)d\tau$ is just the total work W' done by the heater. If (15) is integrated over the same time and a constant is defined by

$$k = \sum_{i=2}\alpha_i b_i^{-1}(\Lambda_i - \Lambda_1\Phi_i^*/\Phi_1^*) \quad (17)$$

then, by comparison with (16), the heat exchange can be written in terms of the observed temperature

$$Q' = \frac{\Lambda_1}{\Phi_1^*}\int_0^t (T^* - T_\infty^*)dt + kW'. \quad (18)$$

THE MEASUREMENT THEORY. EQUIVALENT SOURCES

Since $\Delta U = Q' + W'$, substitution from (10) and (18) gives the equation

$$W' = \frac{C_1}{\Phi_1^*}(T_2^* - T_1^*) - \frac{\Lambda_1}{\Phi_1^*}\int_0^{t_2} (T^* - T_\infty^*)dt - kW'.$$

$$(19)$$

Using (13) we can put (19) in the usual form of an energy equivalent multiplying a corrected temperature rise

$$W' = \left(\frac{C_1}{\Phi_1^*}(1+k)\right)\left[T_2^* - T_1^* + b_1 \int_0^{t_2} (T^* - T_\infty^*)dt\right].$$

(20)

Several points about this equation deserve emphasis: (1) The corrected temperature rise does not depend on the temperature T_1^* being constant; it may be a single exponential function of time. (2) The energy equivalent depends on the position of the thermometer through Φ_1^* and k. (3) The energy equivalent depends on the spatial distribution $g(P)$ through the α_i in k.

One feature of Eq. (20) which is useful experimentally is that the corrected temperature rise must be a constant when the temperature is a single exponential function of time. This constancy can be shown by putting $T^* - T_\infty^* = (T_1^* - T_\infty^*)\exp(-b_1 t)$ and integrating from $(T_1^*, 0)$ to (T_2^*, t_2). Constancy of the corrected temperature rise is therefore a criterion for the single exponential condition.

Equation (20) represents a linear theory—heat capacity and thermal conductivity independent of temperature—and should be adequate for the accuracy required in laser calorimetry. It is a complete measurement theory in that the basic physical law has been reduced to a set of observations to be made in the laboratory. The observed temperature T^* is obtained by some suitable thermometer, b_1 and T_∞^* from two rate observations using (14), and the quantity $C_1[\Phi_1^*(1+k)]^{-1}$ from a known electrical or laser work quantity. These known quantities can then be used in a determination of an unknown quantity, with the most important restriction that the two work quantities have the same relative geometric distribution in the calorimeter, as expressed by the α_i in (15). Since the comparison is between an electric heater and a laser beam, this restriction would destroy the usefulness of the calorimeter but for the idea of equivalent sources.

Equivalent sources are necessary only for evaluating the heat exchange. The change in internal energy, measured in rating periods, is independent of the location of the source. It may be inferred that calorimeters are more accurate if the change in internal energy ΔU is large compared to the heat exchange.

Equivalent sources have been discussed in connection with adiabatic calorimeters.[6,10b] Ideally, the design to make sources equivalent is to force heat from any source inside the calorimeter to reach the surface, where heat is exchanged with the surroundings, at only one point (or through a region of infinite thermal conductivity). The point (or region) can then be treated as a secondary source of heat for heat exchange (α_i is the same for all sources) and the theory outlined above
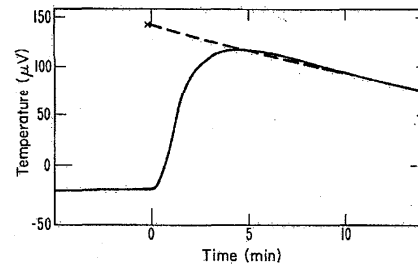

FIG. 2. Temperature-time curve for a one-minute electrical input in an isoperibol calorimeter. The single exponential part of the curve is extrapolated to $t=0(+)$ or to $t=0.5$ min to account approximately for the heat exchange.

evaluates the heat exchange. This idea is especially useful because it can be demonstrated experimentally by electric heaters at different locations and thus, becomes important where the accuracy of measurements may be questioned. The temperature measurement for evaluating the heat exchange must be measured outside of the secondary source.

Laser beams can also be used to demonstrate the equivalence of sources if the fraction of the beam absorbed does not vary with position. The meaning of a negative result is not clear cut. It may imply either dependence of the heat exchange or the fraction absorbed on the location of the source, or some combination.

An important advantage of the secondary source is that the heat capacity and thermal conductivity inside the secondary source need not be independent of the temperature except during the rating periods. If the laser vaporizes the inner surface—a process outside the scope of our linear equations—the measurement may still be valid if the vapor is redeposited inside the calorimeter in its original state.

Thermal radiation from surfaces inside the calorimeter heated by the laser beam cannot be handled readily by the equivalent source technique because the surfaces are heated in a way different from the calibration experiment. The error can be made small by avoiding excessive heating of the surface absorbing the beam and by having the smallest possible solid angle for reradiation to escape from the calorimeter.

The linear theory of (20) may not be adequate for problems requiring high accuracy, although it apparently applies to the very accurate work done in stirred water calorimeters.[12,13] In a nonlinear problem the linear theory might be used to account for a small heat exchange and for a small deviation of the calorimeter temperature from uniformity in the rating periods, but the nonlinear relations of the internal energy to the observed temperature could be determined by several calibration experiments over different parts of the temperature range.

EXTRAPOLATION TECHNIQUES

Extrapolation techniques are sometimes used to analyze data in isoperibol calorimetry. A typical temperature-time curve is shown in Fig. 2 for a calibration experiment with an electrical input lasting one minute. There is obviously a difference between extrapolation to zero time and extrapolation to the mid-point of the electrical input interval. In general, neither extrapolation provides a reliable evaluation of the integral in (15).

The extrapolation technique is nevertheless useful in certain circumstances, but it must not be applied indiscriminately. The first assumption in comparing two sources by extrapolation methods is that they have the same or equivalent geometrical distribution in the calorimeter; that is, they have the same α_i in (15). This point can be investigated experimentally.

We now consider a cw input, starting from a constant temperature T_∞

$$f(\tau) = \beta \quad \text{for} \quad 0 < t < t_1,$$

$$f(\tau) = 0 \quad \text{for} \quad t < 0 t > t_1.$$

The corrected temperature rise ΔT obtained by (20) is

$$\Delta T = b_1 \sum \alpha_i \Phi_i b_i^{-1} \int f(\tau) d\tau. \tag{21}$$

In this case the integral is βt_1. For the temperature during the final rating period we obtain

$$T - T_\infty = (\beta t_1)(\alpha_1 \Phi_1 / b_1 t_1) \exp(-b_1 t) [\exp(b_1 t_1) - 1]. \tag{22}$$

Extrapolation to $t=0$ to get $T_0 - T_\infty$ shows a dependence on t_1, the duration of the input. Of course, this dependence can be removed by applying a correction, since both b_1 and t_1 are known. Comparison of (21) and (22) shows that extrapolation does not account for the heat exchange for the higher order terms, but if the two sources have sufficiently similar geometrical distributions, this difference will be constant and can be evaluated and then used in subsequent data analyses. To estimate the magnitude of the dependence on the duration of the input, the exponential is expanded to give

$$T_0 - T_\infty = \beta t_1 \alpha_1 \Phi_1 (1 + b_1 t_1/2 + \cdots). \tag{23}$$

For a calorimeter having a "cooling constant" $b_1 =$

1/300 sec^{-1}, the comparison of a pulse ($t_1 = 0$) and a 30-second cw input is wrong by 5%. More accurate comparisons can be made by extrapolation of the exponential to $t = t_1/2$. Substitution of this value in (22) and expansion of the exponentials gives

$$\Delta T = (\beta t_1) \alpha_1 \Phi_1 (1 - \tfrac{1}{2}(b_1 t_1) + \tfrac{1}{8}(b_1^2 t_1^2) - \cdots)$$

$$\times (1 + \tfrac{1}{2}(b_1 t_1) + \tfrac{1}{6}(b_1^2 t_1^2) + \cdots). \tag{24}$$

Multiplication and cancellation in (24) gives

$$\Delta T = (\beta t_1) \alpha_1 \Phi_1 (1 + b_1^2 t_1^2/24 + \cdots). \tag{25}$$

Extrapolation to $t = t_1/2$ therefore accounts for most of the dependence on the duration of the power input. It still does not account for heat exchange due to the terms which decay more rapidly.

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[11] The latter assumption holds for a rectangular parallelpiped, a right circular cylinder, [H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, London, 1959), 2nd ed.] and for the two-body model [E. D. West and K. L. Churney, J. Appl. Phys. 39, 4206 (1968)]. It can also be shown for a model consisting of any number of bodies.

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